THE DESTRUCTIVE DISTILLATION OF THE BANANA TREE IN CONNECTION WITH THE UTILIZATION OF POTASH

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Ethelred Erasmus Adolphus Campbell

ENTITLED The Destructive Distillation of the Banana Tree in Connection with the Utilization of Potash.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in General Science.

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TABLE OF CONTENTS.

I

THE POTASH SITUATION.

A little over half a century ago the only source of potash in the United States was wood ashes. During that time, however, the important discovery of the natural deposits of potassium salts in Strassfurt, Germany, were made. The cheapness with which this salt could be obtained not only encouraged its constant importation, but also discouraged the growth of potash industries in this country. Only about one percent of the salts used in this country previous to the world war represented domestic production. This fact is the more appalling when it is recalled that 622,179,164 pounds were imported in 1912 at a cost of $10,692,285 as against 170,555,450 pounds in 1915 at a cost of $3,765,224[1].

The severing of diplomatic relations with Germany and the subsequent declaration of war stopped all imports from Germany, including potash salts. As a result of these conditions, a dire need for these salts was created. The chemists of the country, after careful analyses, suggested numerous sources from which potash salts could be obtained in the United States, the most important being the following:

As by-products from:

1. Wood ashes
2. Bittern from salt manufacture
3. Wool
4. Fish water
5. Sugar factories
6. Cement plants
7. Blast furnace gases

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1. G. C. Baker, A Search for Potassium, p. 1.

As primary products from:

1. Kelp
2. Alunite
3. Western lake waters
4. Feldspar.[1]

As a result of these suggestions, a vigorous prosection of potash manufacture is being conducted throughout the country. Most notable among the producers are perhaps the DuPont Company which is now producing potash from Chili Nitrate[2], and the Nebraska Potash Industry[3]. It is estimated that 720,000 tons of potash salts can be obtained annually from the former, and that Nebraska now produces three times that produced by the whole country in 1916. These facts are encouraging when it is recalled that the total German export of potash salts to all the world before the war was 900,000 tons. While it is not very likely that all the fields suggested will be worked, nevertheless they remain as reserve fields upon which to turn when other fields are depleted.

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1. Met. & Chem. Eng. Vol.XV, p. 508.

2 & 3. Met. & Chem. Eng. Vol. XVIII, p. 248.

A. History of Research on the Banana Stalk.

R. H. Ellis in an article published in the Journal of The Society of Chemical Industries for April, 1916, pp. 456-57, gave the results of his analysis of the ash obtained by burning banana stalk. The percentages of the substances found were as follows:

SrO_2	Fe_2O_3	Al_2O_3	CaO	MgO	K_2O	Soda	SO_3	CO_2	Cl	P_2O_5
9.61	.16	3.49	1.69	1.68	45.90	trace	2.10	31.11	1.52	2.74

Dr. Hanley of Leeds also analysed the stalk and his results compared with those of R. H. Ellis are as follows:

	Ellis	Hanley
Moisture in original stalk.....	91.6%	92.7%
Dried matter in original stalk.....	8.4	7.3
Ash " " "	2.4	1.5
Potash " " "	1.14	0.9
Ash in dried matter in original stalk.....	29.9	20.5
Potash in dried matter in " "	13.73	12.35
" " ash	45.9	59.1

Dr. Hanley also extracted the juice by pressure and found that it contained 0.7% of potash. He also calculates from his experiment that one ton of stalk will give 188 lbs. of dried matter containing 13.7% of K_2O, or 54 lbs. of ash containing 47.5% K_2O, or 25 lbs. of pure potash. In the May number of the Journal mentioned above, Mr. Ellis published the article, "Note on the Presence of K_2O in Banana Skins". His results are as follows:

Moisture in banana skins.....	88.2%
Dried matter in " "	11.8%
Ash " " "	1.77%
Potash " " "	1.05%
Ash in dried matter	15.00%

Potash in dried matter.....9.03%

Potash in ash.....57.16%

Subsequent searches in the literature of the Chemistry and the Agricultural Seminars of the University disclosed in the latter articles by Nemesio B. Mendiola, B.S. and José Dacanay, B.A.,entitled "Composition and Uses of Banana Stems and Leaves" and "The Banana Fruit" respectively. These articles are found in the Philippine Agriculturist and Florester, Vol. 3, No. 4, page 80 for 1914. It seems probable that Ellis and Hanley conducted their researches without having any knowledge of this earlier work. The Philippine research gives the following as the mineral content of the ash:

K_2O	P_2O_5	MnO	CaO	MgO
36.67%	4.28%	.15%	9.59%	1.59%

These authors conclude by saying that "it appears that the most important constituent of the ash is potassium oxide, which constitutes over one-third of the whole". They also found the stalk to contain 1.34% of ash and 0.03% of nitrogen. "A ton of green stalk", they say, "should contain

N	K_2O	P_2O_5	CaO	MgO
0.3 Kg.	4.9 Kg.	0.5 Kg.	1.2 Kg.	0.2 Kg.

Mr. G. C. Baker points out that 45.17% of the ash of the banana stalk consists of K_2O[1].

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1. A Search for Potassium p. 10, Thesis, 1917.

B. Experimental Work.

On June 20, 1917, a research was conducted by the author to extend the knowledge of the potassium content of the banana stalk and also to find out the nature of its distillation products. In a preliminary experiment, 200 grams of a stalk obtained at a grocery store were cut into small pieces and distilled in a 750 c.c. distilling flask. The flask was connected to a condenser, and the condenser to a flask and a Bunsen burner. Heat was applied gently to the flask containing the stalk. The temperature at first rose gradually and distillate came over quite freely. A gas was obtained which burned when the temperature of the flask had reached 276° C. Moisture continued to pass over at a temperature of 330°. Only combustible gases passed over above 365° C. The distillate obtained was 182 c.c. On examining it, it was found to react slightly acid to litmus. Upon titrating 13 c.c. with .113 N KOH, 2 c.c. of the alkali were required for neutralization. The total volume of acid in distillate was found to be 3.164 c.c. of normal acid. The weight of the charred residue was 7.5 grs. or 3.9% of the original stalk, while the moisture and gas together approximate 192.5 grs. or 96.2%.

About 15 lbs. of a mature banana tree were obtained at the green house of the University. Three samples of twenty grams each were taken from different parts of this piece for analysis; that is, from the center stem, from the sheaves around the center stem, and from the leaves. These samples were dried at 120° in an oven in order to determine the amounts of available dried matter. The results were as follows:

	Wt. of Sample	Section of Tree	Dried Matter
(1)	20 grams	center	0.7521 gr. or 3.76%
(2)	20 "	outer sheaves	1.6244 gr. or 8.12%

Wt. of Sample	Section of Tree	Dried Matter
(3) 20 grams	leaf	3.6055 or 18.03%

It was also observed that on exposure to air after drying, these samples absorbed moisture in varying proportions, this fact being observed when the dried samples were being weighed. They absorbed moisture in proportion? to the amount of moisture they had contained. Thus sample 1 absorbed moisture slower than 2 or 3, sample 2 absorbed moisture faster than 1, and sample 3 absorbed moisture very rapidly.

The ash and organic matter obtained were as follows:

Sample	Ash Gr. Wt.	Per Cent.	Organ. Matter
1.	.2991	1.5	.4530 or 2.27%
2.	.1828	.91	1.4416 or 7.2%
3.	.4069	2.03	3.1986 or 15.99%

These samples of ashes were each dissolved in hot water and the filtrates made up to 500 c.c. each. 50 c.c. of each sample were taken and analysed for potassium (volumetrically[1]) after the chlorine was removed with .1 N $AgNO_3$. The percentages of potassium in the ashes of the samples were as follows:

Sample	Potassium Found	Per Cent K in Ash	Per Cent in Sample
(1) 20 gr.	0.148 g.	49.5	.74
(2) 20 gr.	0.07 g.	38.3	.35
(3) 20 gr.	0.188 g.	46.19	.94

About 1000 grams of dried stalk were placed in an iron retort and distilled to obtain the organic content. By means of the salting out process with potassium carbonate, 9 c.c. of a black organic mixture were obtained which boiled as high as 290°.

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1. The cobaltinitrite method of Prof. Burgess and O. Kamm was used. Illinois State Water Survey, 10, 22.

Fifteen pounds of half-dried stalk were distilled in the same retort. 2,420 c.c. of distillate were obtained. By subsequent salting out, 13 c.c. of organic matter were obtained. Considerable NH_3 was given off on salting out with potassium carbonate.

It has been found[1] that when any percentage of a volatile acid is dissolved in water and the solution is distilled, the rate at which this acid passes over with the steam is definitely determined for the particular acid. It is found, furthermore, that if this solution is fractionated and collected in volumes of 10 c.c. each, the amount of alkali required to neutralize the first 10 c.c. is also a constant quantity for the acid in question. The amounts of alkali required to neutralize the 2nd, 3rd, 4th c.c., etc., are also constant quantities for this acid. These constants are known as the Duclaux Constants. Below are the constants for volatile acids having from 1 to 6 carbon atoms.

	C_1	C_2	C_3	C_4	C_5	$C_{4\ iso}$	$C_{5\ iso}$	C_6
1st 10 c.c.	3.95	6.8	11.9	17.9	24.5	25.0	28.7	33.0
2nd 10 c.c.	4.40	7.1	11.7	15.9	20.6	20.9	23.1	24.0
3rd 10 c.c.	4.55	7.4	11.3	14.6	17.0	16.0	16.8	19.0

It is customary to distil 100 c.c. of the acid solution. The constants obtained for the acid in this experiment are given below.

One-half of the alkaline residue was made strongly acid with sulphuric acid and 900 c.c. of the organic acid collected. 750 c.c. of this solution were redistilled and collected in five 150 c.c. portions. The Duclaux constants were obtained and are as follows:

1. Allen's Com. Org. Anal., I, 519.
Note: The constants here given are not those worked out by Duclaux, but those worked out and applied in the course in Qual. Organ. Anal. at the University of Illinois.

Fraction	Constants Obtained
1	10.82 and 10.50
2	8.8 " 8.70
3	8.25 " 8.27
4	7.4 " 7.56
5	6.9 " 6.97

This acid seems to be acetic with a trace of a higher acid. The 22 c.c. of organic matter obtained were dried and distilled twice in order to obtain as nearly as possible constant boiling fractions. The following table shows the boiling points of these fractions, approximate volumes, reaction to litmus, and solubility in H_2O, dil. NaOH, dil. HCl, Con. H_2SO_4, and ether.

Fraction	Boiling Point	Volume	Reaction to Litmus
1.	40°- 70°	2 c.c.	alkaline
2.	70°- 80°	3 c.c.	"
3.	80°- 91°	2 c.c.	"
4.	120°- 160°	3 c.c.	"
5.	160°- 180°	2 c.c.	neutral
6.	180°- 220°	3 c.c.	"
7.	200°- 45°	3 c.c.	"

Fraction	Solubility in H_2O	Solubility in NaOH	Solubility HCl	Solubility H_2SO_4	Solubility Ether
1.	Sol. Basic	Soluble	Soluble	Soluble	Soluble
2.	" "	Appr. Sol.	"	"	"
3.	Slightly	Slightly	Slightly	"	"
4.	"	Insol.	Insol.	"	"
5.	Insol.	Slightly	"	Insol.	"
6.	"	Insol.	"	"	"
7.	"	"	"	"	"

Fractions 1, 2, 3, and 4 were treated with dil. H_2SO_4 and distilled. A small amount of an indifferent neutral substance was obtained. NaOH was added to the residue and the basic portion distilled off. This latter portion (probably amines) was strongly alkaline. On the addition of benzene sulphonyl chloride and subsequent shaking, a variety of colours were observed-- from deep yellow to red. No precipitate was obtained on acidifying with HCl, or on allowing part of the basic solution to stand. The amine is probably a tertiary

one. Phenylhydrazine gave hydrazones with the neutral portions obtained above, while no aldehyde test was obtained with ammoniacal $AgNO_3$. Hence these neutral portions are ketones and not aldehydes. Fractions 5 and 6 gave slight tests with phenyl hydrazine and a slight silver mirror with amm. $AgNO_3$. Hence the presence of the group $-C\begin{smallmatrix}=O\\-H\end{smallmatrix}$.

C. Summary and Conclusion.

The moisture, gas, and organic matter together approximate 96.2 per cent, while the remaining 3.8 per cent contains chiefly potassium and subordinate amounts of other inorganic minerals. The research shows, moreover, that the average percentage of ash obtainable from the banana tree is 1.5. The leaf of the tree stands highest in ash content, the center next, and the sheaves the lowest. The percentage of potassium in the ash shows, however, that the center stands highest with 49.5%, the leaf next with 46.19% and the sheaves third with 38.3%, the average potassium content of the ash being 44.67%. The amount of organic matter obtained on distillation is small.

While it is safe to conclude that the banana tree furnishes an excellent source of potassium, it is by no means safe to say that such an industry could be safely developed in countries to which bananas are shipped. Such an industry is impossible primarily because the stalks which bear the fruit are shipped to various parts of these countries. On the other hand, such a potash industry, if it is to be the most profitably developed, must be developed in those countries where the banana is grown. The large amount of water content could be easily got rid of by allowing the stem to dry in the sun in the tropics where the climate is always warm. Since, however, it has been shown that the center stem contains most of the potassium, the

question may be raised as to whether such an industry could be made profitable even in the Tropics, since a part of this stem is shipped with the fruit. But the answer is clear to those who are acquainted with the banana cultivation that the industry is possible, since the stalk which is shipped rarely, if ever, exceeds one-third of this center stem of the whole tree. The trees are cut down when the crop is harvested. It is very improbable that the tree could become a good source of organic matter, since, as the research shows, this organic content is small indeed. An article in the Textile World Journal, Vol. 53, p. 65, shows, however, that dyestuffs have been obtained recently from the banana stalk.

II RESEARCH ON CORN COB.

Work was also done on corn cob to determine its potassium content and distillation products. 5.5 grams of cob were ignited in a crucible and burnt to ash. The ash obtained weighed .23 grams or 4.2% of the cob. Upon dissolving the ash in water and analyzing with cobaltinitrite solution, it was found to contain .066 gr. potassium or 28.7%.

600 grams of cob were subsequently distilled in an iron retort to get an idea of the quantity of distillable organic matter. The distillate obtained was 240 c.c. which was strongly acid to litmus. 5 c.c. of this solution required 25 c.c. of .113 N KOH for neutralization. Accordingly, the 240 c.c. of distillate contained acid equivalent to 135 c.c. of normal acid. This distillate also contained a large amount of water soluble and water insoluble organic matter. The non-condensable gas burned very freely shortly after the distillation began.

3400 grams of cob were distilled in the same iron retort and

1700 c.c. of distillate collected. The water insoluble portion was separated by a separatory funnel. The water soluble organic portion was obtained by subsequent distillation and salting out, and measured 55 c.c. These 55 c.c. were redistilled and separated into three fractions with boiling points as follows:

Fraction	boiling pt.	volume
A.	45-72°	10 c.c.
B.	72-110°	25 c.c.
C.	110-215°	15 c.c.

Analysis of fraction A gave excellent test for methyl alcohol by forming the methyl ester of 3,5 dinitrobenzoic acid.[1]

Fraction B was found to consist of complex mixtures of aldehydes of high molecular weights. A bright silver mirror was obtained on the addition of a small portion of this fraction to ammoniacal silver nitrate. The same test was obtained for fraction C. The basic portion was separated by the addition of NaOH and subsequent distillation. 5 c.c. of this solution required 1.35 c.c. of .208 N acid for neutralization. No primary or secondary amine test was obtained by the addition of benzenesulfonyl chloride.

The water insoluble portion which measured 65 c.c. was distilled under diminished pressure and separated into the following fractions:

No.	Temp. of Bath.	Temp. of Sol.	Pressure	Volume
1.	125°-130°	40°-75°	14 m.m.	8 c.c.
2.	130° 140°	75°-92°	14 m.m.	6 c.c.
3.	140°-150°	92°-100°	14 m.m.	7 c.c.
4.	150°-166°	101°-115°	14 m.m.	8 c.c.
5.	166°-180°	115°-120°	14 m.m.	6 c.c.
6.	170°-180°	114°-121°	16 m.m.	15 c.c.
7.	180°-195°	121°-132°	18 m.m.	7 c.c.
8.	195°-201°	132°-137°	25 m.m.	6 c.c.

1. Test from Mulliken Identification of Pure Org. Comp. Vol. I, g814

The specific gravities of a few of these fractions were found at a temperature of 21.5° C. and showed a rise with the boiling points of the fractions. Thus fraction 2 had a specific gravity of 1.047; fraction 3, 1.0554; fraction 4, 1.0566.

The following results were obtained on testing fraction 2.

(1) Ignition test: Burns with dense sooty flame.

(2) Analysis: Shows, C, H, O.

(3) Solubility: Insol. in water, acid and alkali. Mostly soluble in con. H_2SO_4.

(4) Boil. pt., 75°-92° at 14 mm; sp. gr. 1.047.

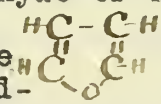
(5) Mainly indifferent oxygen compounds.

Tests: (a) Very faint aldehyde test (But furfural does not give a good test)

(b) .5 c.c. + .5 c.c. acetyl chloride gives black emulsion.

(c) Heated with alkali gave a yellow colour, but not as strong as furfural.

(d) Phenylhydrazine acetate + saturated aq. sol. of unknown gives $>C=O$, test as with furfural but remained liquid; therefore aldehyde or ketone.

(6) Sp. gr. indicates compound of furfural type  Solubility in H_2O is about 2 parts per hundred.

The reactions of the fractions toward amm. silver nitrate and toward phenylhydrazine acetate show that fraction 1 to 5 are principally aldehydes. Strong silver mirrors were obtained in all of these fractions. The intensity of the mirrors decreases, however, from 5 to mere faintness in 8. Yellow emulsions were obtained with fractions 1 to 4, slight reaction with 5, and no reaction with 6 to 8.

The organic acid was extracted by acidifying the alkaline solution with H_2SO_4 and subsequent distillation. 750 c.c. of this solution were redistilled and collected in five fractions which had the following strengths and Duclaux Constants.

Fract. & Vol.	Vol. Used.	c.c. of .111 N KOH reqd.	Constants obtained.
(1) 150 c.c.	5 c.c.	27.25 c.c.	7.54 and 7.85
(2) 150 c.c.	5 c.c.	29.2 c.c.	7.5 " 7.9
(3) 150 c.c.	5 c.c.	32.45 c.c.	7.8 " 7.85
(4) 150 c.c.	5 c.c.	37.95 c.c.	7.7 " 8.2
(5) 115 c.c.	5 c.c.	52.3 c.c.	6.8 " 7.4
		Average constants	7.45 and 7.86

These constants are well within the limits for acetic acid.

CONCLUSION

The research shows, therefore, that corn cob contains a fair percentage of potassium in the ash; that it gives a fair yield of methyl alcohol, a large yield of acetic acid; and a large amount of water insoluble organic oil which is chiefly aldehyde in nature. Although the percentage of potassium is smaller than that of banana stalk (44.67% in the former and 28.7% in the latter), the amount of ash in corn cobs is nearly three times as large as in banana stalk. Consequently, it seems to be even a better source of potassium. Nor is there any reason to doubt that one could look to corn cobs as being a favourable source of wood alcohol and acetic acid. Finally, the richness of the cobs in organic matter makes it reasonable to believe that further researches will be conducted on it partly because of its commercial possibilities, and partly because of its interest in itself.

III REACTIONS OF QUINONES.

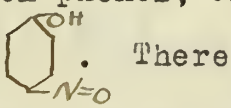
A. Theoretical Part.

The quinones, or 1,4 diketones of the aromatic series, have long been of extreme interest to organic chemists. The structure of these compounds, though now fully and unquestionably established, gave rise to a great deal of controversy. The early objection to the ketonic nature and structure of these compounds was due partly to the fact that they differed from the ordinary ketones in a number of ways, partly because of some of their peculiar reactions to form other compounds; and partly to the lack of knowledge relative to the tautomerism of heterocyclic compounds. Because of the oxidizing property of the quinones, Graebe early favoured the peroxide formula for benzoquinone,  . Such a formula is by no means compatible with the facts based upon the following general methods of preparation:

(1) The Oxidation of aniline.

(2) The oxidation of hydroquinone.

(3) The oxidation of p-aminophenol and

(4) The oxidation of p-diaminophenol. From the structures of the above compounds, it is clear that the quinone is ketonic in structure. Furthermore it is possible to prepare chloranil, $C_6Cl_4O_2$ by (substituting chlorine) and hexachlor benzene from the latter by the action of PCl_5[1] . The ketonic structure, therefore, is the more favourable one. With hydroxylamine the mon- and dioxime are also formed. The monoxime is also prepared by the action of nitrous acid on phenol, and is also called p-nitroso phenol with the formula  . There is some question, however, as to whether or not the oxime formula should always be assigned to this compound. But such a question is not wholly

1. Graebe, Zeit. für Chem. 3, 39.

warranted as the experimental part of this work shows, which makes it necessary that the reactions involved must be explained primarily in terms of the phenomenon of tautomerism.

B. Experimental Part.

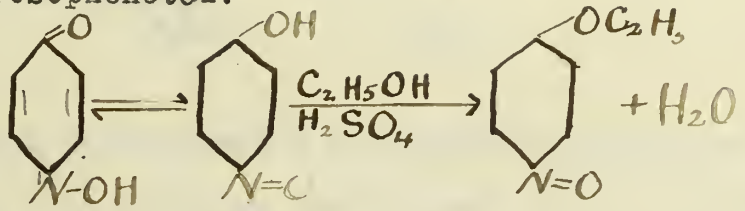
Preparation of p-nitrosophenole from Phenol by the action of $NaNO_2$ in the presence of H_2SO_4.[1]

A mixture of 400 grs. of con. H_2SO_4 in 400 c.c. of water were dropped slowly into a mixture of 60 grs. of phenol, 27 grs. NaOH, and 54 grs. $NaNO_2$ dissolved in 1000 c.c. of H_2O containing 500 grs. of ice. The mixture was shaken constantly during the process and for half an hour after the solutions were mixed. The p-nitrosophenol separated out in crystals. The mixture was allowed to stand in the cold for two hours and then filtered, dried and used for further experiments.

Preparation of p-nitrosophenetol from p-nitrosophenol[2]

To 50 c.c. of absolute alcohol 4 c.c. of con. H_2SO_4 were added gradually and the mixture cooled to room temperature. 10 grs. of p-nitrosophenol were then added gradually and the solution shaken constantly. This solution was then allowed to stand for ten minutes and then poured into 200 c.c. of cold water. The p-nitrosophenetol was extracted with 50 c.c. of ether and washed with 60 c.c. of 5% NaOH solution and finally with H_2O. The ether solution was allowed to evaporate spontaneously on a watch glass leaving the dark green crystals of p-nitrosophenetol.

Reactions.



1. Beilstein Vol. 2 Pt. 1, p. 677.
2. See thesis of I. N. Hultman, June, 1917.

Preparation of p-nitrosoanisol.

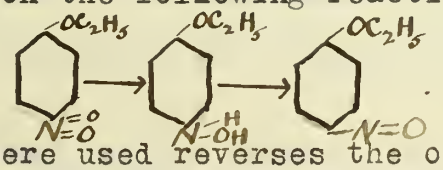
The preparation of this compound was effected in identically the same way as the above compound.

Preparation of p-nitrosophenylpropyl Ether.

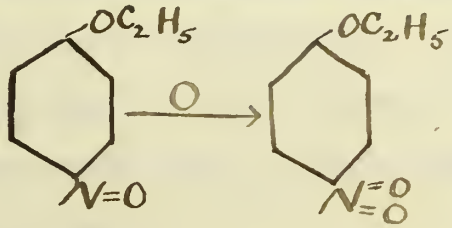
To 10 c.c. of propyl alcohol, 4/5 c.c. of con. H_2SO_4 were added and the solution cooled to room temperature. 2 grs. of p-nitrosophenol were added gradually and the solution shaken and allowed to stand for 10 minutes. The solution was then poured into 40 c.c. of H_2O and the propyl ether extracted with 10 c.c. of ether. This solution was washed with 12 c.c. 5% NaOH and then with H_2O. The ether was allowed to evaporate spontaneously but the nitroso ether did not crystallize even on standing over night. The liquid was of a dark green color. The yield was .9 grams. This propyl ether is light green after it is steam distilled.

Oxidation of the p-nitroso to p-nitro ethers by means of con. HNO_3.

The older method of preparation of nitroso derivatives of phenol ethers was based on the following reactions:



The method here used reverses the old process and prepares the p-nitro ether from the nitroso compound according to the following reactions:



Procedure.

One gram of p-nitrosophenetol was added in small portions to 20 c.c. of con. HNO_3. The solution was stirred during the addition. It was then allowed to stand for ten minutes. The solution was then

poured drop by drop into 50 c.c. of cold H_2O shaking constantly. A fine crystalline reddish pink precipitate was obtained which melted at 60° before recrystallization. Upon recrystallization and purification with bone black a cream colored product was obtained. Its melting point was 59°- 60°. Yield, 1 gram. The melting point correponds to that found in Beilstein for this ether.

The p-nitrosoanisol was prepared in a similar way and was found to be on recrystallization, a light yellow product with a melting point of 54°.

The p-nitrosophenylpropyl ether obtained above was poured drop by drop into 4 c.c. of con. HNO_3, and the solution treated as in the above two experiments. A dark red oil separated out on pouring it into 20 c.c. H_2O. The oil was extracted with 10 c.c. of ether, washed with H_2O made alkaline with 5% NaOH, dried with $CaCl_2$ and filtered (.2 c.c. were obtained. Its boiling point was 285°-287°.

The method of Rising[1] was used in an attempt to prepare the corresponding hydroxylamine of p-nitrosophenetol, but in every case the yellow azoxy compound was obtained. It was observed that the yellow crystals begin to separate at a temperature of 40° C.

Summary of Part III.

A new method has been used for the preparation of nitroso and nitrophenyl ethers. The p-nitrosophenetol and anisol are prepared directly from p-nitrosophenol by the action of ~~ethyl~~ alcohol and sulphuric acid. Subsequent oxidation of the nitroso ethers with nitric acid yielded the nitro ethers.

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1. Berichter 37, 43.

It was hoped that the phenylhydroxylamines corresponding to the three nitroso ethers could be prepared by reducing the nitroso compounds, but attempts to do this were unsuccessful.

The p-nitrosophenylpropyl ether and the nitro ether have been prepared for the first time by the same method used for the methyl and the ethyl ethers.

The old method of preparing the p-nitrosophenetol and the anisol from the nitrophenetol and anisol by reduction of the nitro compounds first to the hydroxylamine, followed by oxidation of the latter to the nitroso compounds, has been reversed. The nitrocompounds were prepared by direct oxidation of the nitroso compounds.

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